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Development of method for the speciation of inorganic iron in wine samples

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ABSTRACT

In this paper, we proposed a procedure for the determination of iron(II) and total iron in wine samples employing molecular absorption spectrophotometry. The ligand used is 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (Br-PADAP) and the chromogenic reaction in absence or presence of ascorbic acid (reducing agent) allows the determination of iron(II) or total iron, respectively. The optimization step was performed using a multivariate technique (Box Behnken design) involving the factors pH, acid ascorbic concentration and reaction time.

The method allows the determination of iron(II) and iron(III) in wine samples, with limits of detection and quantification 0.22 and 0.72 $\mu g\,L^{-1}$, respectively. The precision expressed as relative standard deviation (R.S.D.) was 1.43 and 0.56% (both, $n = 11$) for content of iron(II) in wine samples of 1.68 and 4.65 $mg\,L^{-1}$, and 1.66 and 0.87% (both, $n = 11$) for content of total iron in wine samples of 1.72 and 5.48 $mg\,L^{-1}$.

This method was applied for determination of iron(II) and total iron in six different wine samples. In these, the iron(II) content varied from 0.76 to 4.65 $mg\,L^{-1}$ and from 1.01 to 5.48 $mg\,L^{-1}$ for total iron. The results obtained in the determination of total iron by Br-PADAP method were compared with those that were performed after complete acid digestion in open system and determination of total iron employing FAAS. The method of regression linear was used for comparison of these results and demonstrated that there is no significant difference between the results obtained with these two procedures.

1. Introduction

Iron is a mineral element present in wine in the concentration range 0.5–25.0 $mg\,L^{-1}$ and is important to the wine technologist because it may cause cloudiness or a colour change when present in a large excess [1–3]. If wine is kept under airtight conditions, iron, being in a reducing medium, exists exclusively as iron(II) and is soluble even if present in large amounts [4]. However, when wine is aerated, the dissolved oxygen oxidizes the iron(II) to iron(III), which is responsible for the precipitation of colouring matter (blue casse) and for the cloudiness in white wines (white casse). Cacho et al. studied the influence of iron, copper, and manganese on wine oxidation, measuring the evolution of different compounds sensitive to this process, such as: anthocyanins, tannins, total phenol content and acetaldehyde. They concluded that the oxidation depends directly of the concentration of these cations in the wine [5]. Oszmianski et al. studied the oxidation process of (+)-catechin in wine-like model solutions in presence of iron(II) ions. They observed that the rate of cat-

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echin oxidation and the extent of browning increase with the iron level. Colourless compounds and yellow pigments are formed in larger amounts at higher iron concentrations [6].

This way, methods for iron speciation in wines are opportune and several procedures have been performed for the determination of iron species in wine samples [7–15]. Valcarcel and co-workers [7] performed an on-line system for the determination of iron in wine, based on the ferro(III)-thiocyanate complex. Wang and Mannino [8] established a method employing adsorptive stripping voltammetry for the determination of iron(III) and total iron in wines. Ajlec and Stupar [9] performed a method using ion exchange chromatography and flame atomic absorption spectrometry (FAAS) for the determination of iron(II) and iron(III) in wine. Weber [10] used a high-performance liquid chromatography (HPLC) system coupled with an electrochemical detector for the determination of iron(II) and another on-line system employing FAAS for the determination of total iron in wine. Perez-Conde and co-workers [11] proposed a flow-through fluorescent sensor for the determination of iron(III) and total inorganic iron in wine. Costa and Araujo [12] proposed a sequential method for the determination of iron(III) and total iron in Portuguese table wines by sequential injection analysis (SIA) employing FAAS. Paleologos et al. [13] performed a procedure for the determination of free and bound iron in wines using cloud point extraction and FAAS. Riganakos and Veltsistas [14] compared two spectrophotometric procedures proposed for the determination of the total iron wines. Stafilov and co-workers [15] proposed methods for the determination of iron(II), iron(III) and organically bounded iron in wines using for separation liquid–liquid and solid-phase extraction.

The iron(II) reacts with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (Br-PADAP) forming a complex, which has absorption peaks at 560 and 748 nm [16,17]. The absorption at 748 nm is lower than at 560 nm, however, at 748 nm the method is completely selective for iron(II). Br-PADAP reacts also with iron(III) forming a complex that has an absorption peak at 560 nm. Both complexes are stable and some procedures have been proposed involving separation and determination of iron(II) and iron(III) using this reagent [18–20]. Oszwaldowski et al. performed procedures for the separation of complexes of iron(II) and iron(III) with Br-PADAP employing micellar electrokinetic chromatography [18] and capillary electrophoresis [19]. A method using Br-PADAP was developed for the simultaneous determination of iron(III) and iron(II) in water samples employing reverse-phase liquid chromatography for the separation of the complexes [20]. Wang and Song [21] used Br-PADAP in method proposed for spectrophotometric determination of iron(III) in irrigation water.

Box Behnken design is a chemometric tool used for optimization of experimental conditions [22–24]. However, the use of this design is still few widespread in analytical chemistry. In recent years, several analytical methods have been optimized using this tool [25–27].

In the present paper, we proposed a procedure for the speciation analysis of inorganic iron in wine. It is based on the reactions of iron(II) with Br-PADAP in the absence and also presence of a reducing agent (ascorbic acid) for the determination of iron(II) and total iron, respectively. The optimization step was performed using a Box Behnken design. The method was applied for the determination of iron(II) and total iron in several wine samples.

2. Experimental

2.1. Instrumentation

Spectrophotometric measurements were made in a Cary 5E UV-visible Spectrophotometer (Varian) with 1.00-cm glass cells.

A Varian model SpectrAA 220 FS flame atomic absorption spectrometer (Mulgrave, Vistoria, Australia), equipped with a deuterium background corrector and automatic switching of hollow-cathode lamps was used. The iron hollow cathode lamp was operated with a current of 5.0 mA. The analytical wavelength at 248.3 nm was used with a spectral bandwidth of 0.1 nm. An air–acetylene flame was used with an acetylene flow rate of 2.0 L min^{-1}, an airflow rate of 13.5 L min^{-1} and a burner height of 13.5 mm.

2.2. Reagents

All reagents were of analytical grade unless otherwise stated.

Ultrapure water was obtained from an EASYpure RF purification system (Barnstedt, Dubuque, IA, USA). Nitric and hydrochloric acid were of Suprapur® quality (Merck, Darmstadt, Germany). Nitric and hydrochloric acid solution were prepared by direct dilution with water from the concentrated Suprapur® solutions.

Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution. Before use, the glassware was rinsed with desmineralized water and dried in a dust-free environment.

Calibration solutions were prepared from 1000 mg L^{-1} iron stock solutions (Merck) by appropriate dilution with a 1% (v/v) nitric acid solution.

2.3. Reagents

2.3.1. Iron (II) solutions

Stock solution (0.50 g L^{-1}) of iron(II) was prepared by dissolving $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (Merck) in 2% (v/v) hydrochloric acid solution (boiled recently). Working standard solutions were prepared daily by stepwise dilution of the stock solution with desmineralized water also boiled recently.

2.3.2. Br-PADAP solution

A 0.05% Br-PADAP solution was prepared by dissolving 0.05 g of Br-PADAP in 3.2 g of Triton X-100 in 10 mL of ethanol and diluting to volume with ethanol in a 100 mL volumetric flask.

Acetate buffer solution (pH 5.5) was prepared by dissolving 74.54 g of sodium acetate (Merck) and 5.2 mL concentrated acetic acid (Merck) with desmineralized water and diluting to 1 L.

Ascorbic acid solution (0.10%) was prepared daily by dissolution of this reagent in water.